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Analysis of the chromium concentrations in cement materials

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Abstract

Chromium is an indelible non-volatile trace element of raw materials used in cement clinker production. This work is focused on the study of the content of total chromium and soluble hexavalent chromium in cements. Cements samples of various types (CEM I, CEM II, CEM III and CEM V) were investigated in the experiment. Total chromium content in cements as well as the chemical composition of cement samples was measured by using X-ray fluorescence spectrometry (XRF). The average concentrations of the total chromium in cements vary from 178.5 to 257.3 mg per kg of cement. The concentration of the soluble chromium (VI) was measured in cement leachates using colorimetric method. The average concentrations of hexavalent chromium ranged from 0.5 to 2.46 mg/kg. The results of chromium (VI) measurements in water leachates confirmed that only a small part of total chromium was extracted from the cement into the water environment. The percentage of water soluble chromium (VI) varied from 0.19 to 1.38 %. In addition, X-ray powder diffraction and (XRD) and infrared analysis (FTIR) were used for the cements investigation. Summarizing the results of chromium (VI) monitoring, approximately 75 % of investigated cements fulfilled the Slovak eco-labelling requirement.

Keywords: Cement; chromium; XRF spectrometry; cement leachates

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1. Introduction

Cement as a basic material for building and civil engineering construction affects the environment not only during its production, but also in the process of its consumption causing a negative impact on both the environment and human health. Heavy metals belong to the most significant hazardous elements presented in cement and cement compounds. These toxic elements originate mainly from the raw materials, but also from refractory bricks lining the kiln, mineral admixtures or the grinding media (normally high-chromium white cast iron) in the final finishing mills [1].

Chromium is an indelible non-volatile trace element of raw materials (clay, limestone and iron additives in particular) used in cement clinker production [1]. Chromium is one of the 25 most widespread elements in the Earth's crust and it is present in raw materials mentioned above in the form of chromium (III). Naturally occurring chromium (III) is not initially harmful, since it is chemically stable. Only at high temperatures found in cement rotary kilns, inert trivalent chromium oxidizes to form reactive hexavalent chromium [2]. According to method based on the fully dissolving of Cr (VI) in an acidic solution, it was estimated that the content of Cr (VI) in cement samples is about 50–90 % of the total Cr content [3]. Hexavalent form of chromium is harmful and allergenic and it is present in the cement, forms water-soluble compounds and has the capacity to penetrate human skin, causing chromium dermatitis, also known as cement itch. Skin contact with cement is considered to be the most common cause of chromium dermatitis [4].

This paper aims to present the results of the study of both total chromium and hexavalent chromium contents in several types of commonly used cements in Slovakia.

2. Materials and Methods

2.1. Materials

The most often used types of cements of selected Slovak producers were assessed in this study. The cement samples of type CEM I - Portland cements, CEM II - Portland composite cements, CEM III - Blastfurnace cements and CEM V – Composite cement were chosen for the experiments. The more detailed characteristics of studied cement composition are in Table 1.

Table 1. The characteristics of the assessed cement types [5]

Type of cements	Characteristic
CEM I 42.5 N	Portland cement - contains mainly clinker and no other single constituents
CEM II/A-S 42.5 N	Portland-slag cement: Portland cement with up to 20 % of blastfurnace slag
CEM III/A 32.5 N	Blastfurnace cements: Portland cement with more than 35 % of blastfurnace slag
CEM V/A 32.5 R	Composite cements: Portland cement with more than 35 % of blastfurnace slag and pozzolana or fly ash

2.2. Methods

The basic chemical composition of tested cements as well as the total chromium content was investigated by X-ray fluorescence analysis (XRF) using SPECTRO iQ II (Ametek, Germany) with SDD silicon drift detector with resolution of 145 eV at 10 000 pulses. The primary beam was polarized by Bragg crystal and Highly Ordered Pyrolytic Graphite - HOPG target. The samples were measured during 300 s at voltage of 25 kV and 50 kV at current of 0.5 and 1.0 mA, respectively under helium atmosphere by using the standardized method of fundamental parameters for cement pellets. Cement samples were prepared as pressed tablets of diameter 32 mm by mixing 5 g of cement and 1 g of dilution material (M-HWC) and pressed at pressure of 0.1 MPa/m^2.

Infrared spectroscopy with Fourier transformation (FTIR) was used for the cement samples characterization in terms of functional groups qualitative analysis. FTIR measurements were performed using a Spectrometer Alpha-T (Bruker, Germany) with ATR technique allowing the direct measurements of powder samples without KBr tablets preparation. Measurements proceeded in transmittance mode, in the range 400 – 4000 cm^{-1} with resolution of 4 cm^{-1}.

XRD experiments were performed using a D2 PHASER X- ray powder diffractionmeter (Bruker, Germany) using Cu $K\alpha$ radiation generated at 10 mA and 30 kV. All scans were performed on powdered samples. The powders were placed on glass microscope slides and placed in the diffractionmeter. Scan conditions were identical for all samples with the step size of 0.02° over the range 2θ from 10 to 70°.

The content of soluble hexavalent chromium was determined in cement leachates. Cement leachates were prepared in accordance to STN EN 196-10 [6]. The same amount of cement and of ultra-pure water (Rodem 6) with conductivity of 5.72 μS/cm and pH of 6.81 was mixed during 15 minutes at laboratory temperature. The prepared cement paste was separated by vacuum filtration through the glass filter with porosity 4 (Morton). The obtained filtrate was adjusted to final volume of 250 mL. The determination of chromium (VI) was based on the reaction of hexavalent chromium with diphenylcarbazide by forming the purple colored compound. The amount of soluble hexavalent chromium was growing with the intensity of purple color. The concentrations of hexavalent chromium in liquid samples were measured by DR 2800 Hach Lange spectrophotometer at 540 nm.

3. Results

The basic components of tested cement samples measured by XRF spectroscopy expressed in form of oxides in weight % are presented in Table 2.

Table 2. The chemical composition of studied cements

Oxides (% mass)	CEM I 42.5N	CEM II/A-S 42.5N	CEM III/A 32.5N	CEM V/A (S-V) 32.5R
MgO	3.823	4.230	6.317	3.751
Al_2O_3	4.390	4.313	5.444	9.571
SiO_2	19.65	20.97	28.78	37.91
SO_3	3.171	3.082	2.716	2.577
K_2O	0.583	0.529	0.526	1.003
CaO	58.15	55.86	48.41	40.06
Fe_2O_3	3.245	2.643	1.706	5.205
TiO_2	0.212	0.217	0.236	0.324
P_2O_5	0.093	0.081	0.055	0.141

The chemical composition of investigated cement samples correlate to the standard chemical composition of particular cement types [7]. The difference in the basic components percentage for tested cement types depends on their composition. CEM I cement contents mainly clinker, other studied cement types include various other components such as blastfurnace slag, puzolana or fly ash.

The presence of chromium as well as other metals was confirmed in studied cements samples by XRF as it is illustrated in Fig. 1.

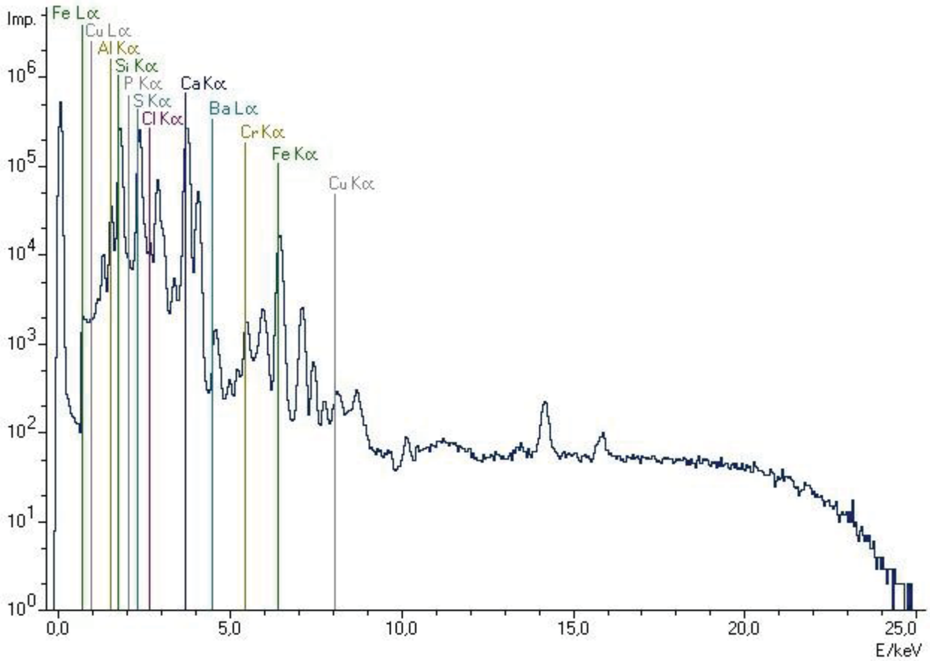

Fig. 1. XRF spectrum of CEM I cement

Considering the fact that chromium (III) originating from the raw materials is oxidized during burning process to chromium (VI) and based on the literature knowledge of $CaCrO_4$ and $CaCrO_4 \cdot 2H_2O$ compounds occurring in Portland cements [8], the presence of chromates ($CrO4^{2-}$) in cement samples was investigated by both XRD and FTIR analyses. Fig. 2 presents the evolution of the XRD patterns obtained on cements samples.

Obviously, the spectrum represents the basic mineralogical phases of cement samples. The results of mineralogical analysis are different from each other tested samples. CEM I cement contents mainly clinker and cement types of CEM II, CEM III and CEM V contain fly ash and blast furnace slag up to a content of 20 to 80 % by weight. Apart from the main crystalline phases, these materials also contain amorphous constituents. These phases therefore also have to be taken into account when quantifying the cement types [9].

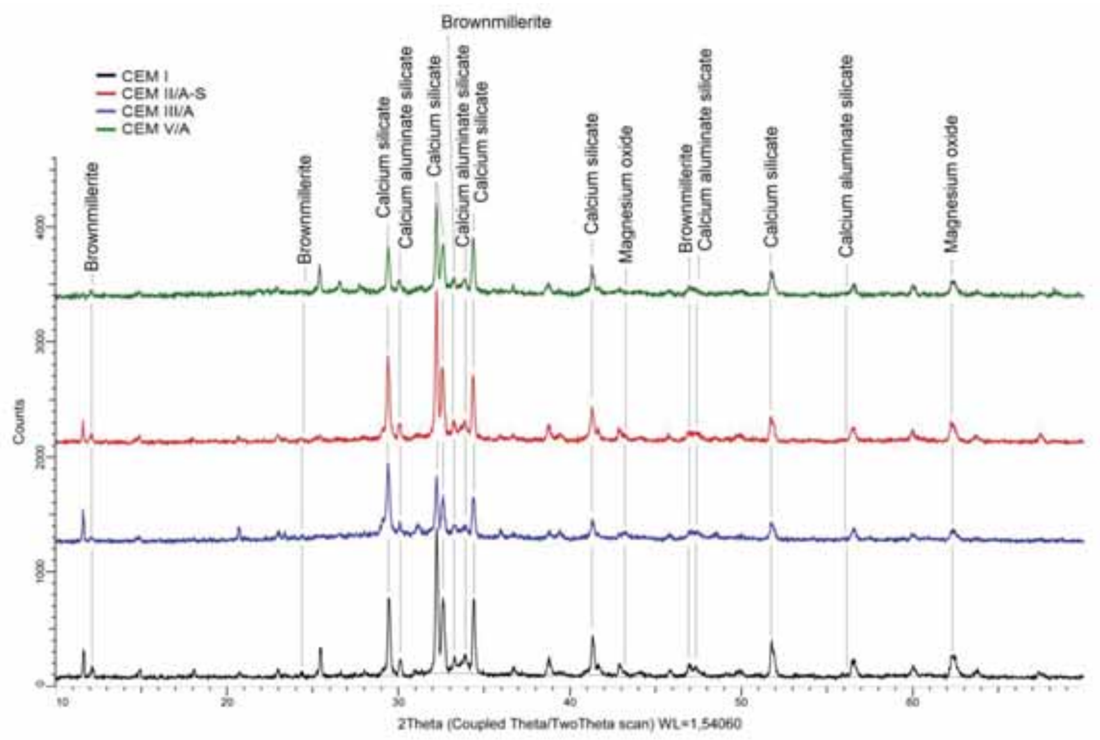

Fig. 2. XRD spectrum of tested cements

In spite of the expectation, the presence of chromates was not confirmed by XRD probably due to very low chromium concentrations. Authors in [8] presented that the presence of chromates was identified by XRD only on samples immersed into 50,000 mg/L of Cr before the diffraction analysis. Ordinary Portland cement (OPC) was more efficient from an initial Cr (VI) concentration of 2,000 mg/L in alkaline-based solution and 5,000 mg/L in water-based solution OPC [8].

As a result of work over the past few years it is now possible to analyze up to 12 phases of Portland cement (CEM I) with a high degree of accuracy [9]. Nevertheless a quantification of these phases is possible by adding a defined amount of a crystalline standard material. The amorphous parts of cements containing slag or fly ash can be determined with an estimated precision of ±2wt. % for amounts higher than approximately 10wt. % [9].

The results of the cement samples FTIR analysis in order to confirmation of the presence of chromate functional groups are presented in Fig. 3.

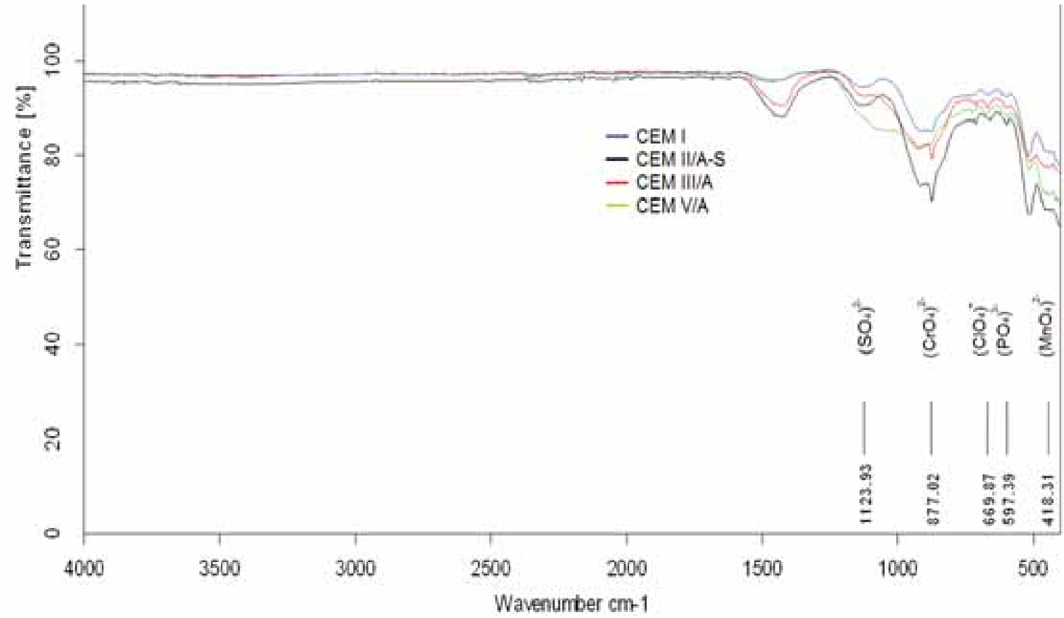

Fig. 3. FTIR spectrum of tested cement types

The major vibrations were detected in the range of 450 – 1500 cm^{-1}. Transmittances associated with cements sulphate (near 618 and 1123 cm^{-1}), chromate (877 cm^{-1}), phosphate (597 cm^{-1}), perchlorate (669 cm^{-1}) and permanganate (418 cm^{-1}) functional groups were observed. Observed vibrations of functional groups were discussed in accordance with [10]. The main vibration of carbonate, usually a symmetric double band at 1420-1450 cm^{-1}, is showed as a widening and overlapping band (1470 cm^{-1}) due to small content of aragonite. As it is seen in Fig. 3, the chromates were confirmed in all tested types of cement samples.

Measured water-soluble chromium concentrations as well as the total chromium concentrations in tested cement pellets are summarised in Table 3. The leaching ratio calculated by comparison of the total and water-soluble chromium is also included.

Table 3. Chromium content in cement pellets and in cement leachates

	pellets	leachates	leaching ratio
	(mg/kg)	(mg/kg)	(% mass)
CEM I 42.5N	178.5	2.46	1.38
CEM II/A-S 42.5N	192.3	1.26	0.66
CEM III/A 32.5N	215.8	0.66	0.31
CEM V/A (S-V) 32.5R	257.3	0.50	0.19

The water soluble chromium (VI) average concentrations vary from 0.50 to 2.46 mg/kg of cement (Table 3). Determination of the water-soluble fraction of Cr (VI) measured in Swedish [11] and Australian cements [12] are reported to be ranging from 0.2 to 20 mg/kg. The same procedure applied for the determination of total chromium and water-soluble chromium contents in commercial cements of Spain [4] reported results of 0.1–7.5 mg/kg.

The concentration of soluble chromium (VI) in cement depends on the clinker content in cement. The sample of CEM I - Portland cement, which has the highest content of chromium (VI), contains only clinker as an important natural source of chromium. CEM III and CEM V cement types contain the least content of clinker but they contain high amount of slag and therefore the concentration of soluble chromium (VI) is lower in these samples.

Cements are one of the building product groups in the Slovak Republic for which the required criteria are stated and the national eco-label is possible to obtain. The maximum value of soluble chromium (VI) content in cements relating to the Slovak eco-labelling process is 1.8 mg chromium (VI) per 1 kg of cement (1.8 ppm) [13]. Content of chromium in tested CEM I cement type (2.46 mg/kg) was higher than eco-labelling limit. The others tested cement types with chromium concentration from 0.5 – 1.26 mg/kg fulfil the eco-labelling requirements related to the concentration of chromium (VI).

The results of measurements chromium content in water leachates showed that only a small part of total chromium was extracted from the cements into the water environment. The minimum chromium leaching ratio (0.19 %) was detected for CEM V cement and the highest one for CEM I cement (1.38 %) –Table 3. As reported in [14], Cr (VI) compounds represented between 30 and 80 % of the total chromium in South African cement clinkers and only 8–26 % of the amount of Cr (VI) species was observed to be water soluble. According to the work [3] there was estimated that the content of Cr (VI) in cement samples was about 50–90 % of the total Cr in an ordinary Portland cement samples.

4. Conclusion

The analysis of the chromium presence in commonly used cements of various producers in the Slovak Republic was performed. Content of total chromium in the cement samples varied from 178.5 to 257.3 ppm. The presence of hexavalent chromium in cements was confirmed by XRF and FTIR methods as expected. The content of water soluble Cr (VI) was measured in the range 0.50 - 2.46 ppm representing approximately 1 % of total chromium content. Taking into account those facts, the more detailed investigation of both total chromium and hexavalent chromium occurrence and its mobility is needed in our further research.

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